



FORMALDEHYDE

AND ITS APPLICATIONS



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AND ITS APPLICATIONS



SYNTHITE LIMITED

MANUFACTURERS OF FORMALDEHYDE:-

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FORMALDEHYDE

A BRIEF SURVEY OF ITS CONSTITUTION, CHEMISTRY, AND INDUSTRIAL APPLICATIONS

FORMALDEHYDE was hardly known commercially until the last decade, although it had been studied assiduously in the laboratories of academic chemists who were attracted by its remarkable properties and its power to react with all manner of substances.

In addition to its utility in organic syntheses, the work of many investigators has suggested its probable fundamental importance in biochemistry, since there is strong evidence that the primary product in the assimilation of atmospheric carbon dioxide by plants, under the influence of sunlight, is formaldehyde, this being subsequently built up by further intricate biochemical processes, into plant tissue.

A great impetus was given to the commercial production of formaldehyde by the discovery by Dr. Baekeland that valuable resinous materials could be obtained when formaldehyde and carbolic acid were allowed to react under suitable conditions. This original discovery of Dr. Baekeland has resulted in much intensive work and the use of synthetic resins has now extended so enormously that they are to be found in every department of home and industry. The pure resins are used for paints and varnishes, also, after hardening, for transparent and semi-transparent fancy goods. When mixed with suitable fillers, such as wood meal or paper pulp, mouldings of the most intricate shapes can be produced rapidly and expeditiously, and as the finished moulding is unaffected by heat, moisture, or chemical action, and furthermore is an excellent insulator, it has obvious advantages over metal which manufacturers, especially of electrical goods, have not been slow to realise. The synthetic resin industry, however, is far too extensive to more than mention it here, but some further information regarding the more interesting developments in this field will be found later in this booklet under "Resins."



Formaldehyde is manufactured principally by a process which is similar to the basic reaction discovered by Hofmann in 1867. Hofmann found that if a spiral of hot platinum or copper wire were held over a vessel containing warm methyl alcohol, the wire continued to glow in the mixture of alcohol vapour and air, pungent fumes being evolved which were afterwards identified as formaldehyde gas. Hofmann termed this process of oxidation "flameless combustion" and it is this "burning without flame" which, after many years arduous research and technical development has been harnessed to the needs of the chemical industry. Thousands of tons of methyl alcohol are now "burnt" annually under carefully controlled conditions by formaldehyde manufacturers, whose ever present problem is how to maintain the combustion within the very narrow limits necessary to ensure the production of formaldehyde, and not worthless by-products.

Many alternative catalysts to the platinum and copper originally employed by Hofmann and collaborators have been proposed and used, but much further research will be required before the theoretical yield of formaldehyde from methyl alcohol is obtained commercially.

 **PROPERTIES.** Pure formaldehyde is a colourless gas at ordinary temperatures and pressure, but it can, with difficulty, be converted to a liquid at $-20^{\circ}\text{C}.$, though this easily changes into a solid modification.

There are obvious difficulties in handling and transporting the pure gas, so manufacturers have taken advantage of the great solubility of formaldehyde in water and it is usually sold as a 40% aqueous solution, this being the strongest which can be handled satisfactorily, and each gallon contains 4-lbs. formaldehyde gas. If this solution is properly prepared it will keep indefinitely at normal temperatures, but if stored in a cool place it is liable to become turbid, and on prolonged standing throws down a voluminous white gelatinous deposit. This precipitation may be prevented by the addition of methyl or ethyl alcohol, and in all commercial formaldehyde a small amount (7—10%) of alcohol is always added in order to ensure good keeping qualities.



The white precipitate is composed of associated molecules of formaldehyde loosely combined with water, and if the material is not too old the solution may be cleared by gentle warming, when it regains its original properties with its reactivity unimpaired.

The addition of sufficient alcohol to prevent this polymerisation and precipitation naturally means increased cost to the formaldehyde manufacturer, and cheap grades of formaldehyde should be viewed with suspicion since it is extremely probable that the alcoholic content has been reduced below the safe margin for good keeping qualities.

Before the advent of synthetic resins into commerce the formaldehyde on the market was practically exclusively of foreign manufacture and varied enormously in formaldehyde and alcoholic content. The solutions available were considered to be "Commercial 40%" if they contained between 38% and 40% formaldehyde gas, and even lower tests have been recorded. Even the British Pharmacopœia (1914 edition) allowed a considerable margin and actually did not recognise 40% material, the specification requiring the solution to contain between 36% and 38% formaldehyde. This however has been amended in the latest (1932) edition.

It will be appreciated that this deplorable lack of consistency greatly increased the already tremendous difficulties which the research workers in the synthetic resin industry had to face, and SYNTHITE LIMITED realising this fundamental fact have endeavoured always to maintain a high standard of uniformity in their product. When SYNTHITE LIMITED commenced production nearly fifteen years ago it was stipulated that their formalin should contain 40.2% HCHO with a tolerance not exceeding 0.1%, that is, not less than 40.1% and not more than 40.3% formaldehyde; the methyl alcohol present being maintained between 9.5% and 10% to ensure freedom from polymerisation under all normal conditions. This specification has always been rigidly adhered to, the extra expense and care taken having been fully justified by the respect which SYNTHITE formaldehyde commands throughout the trade.



The astounding increase in formaldehyde consumption has resulted in intensive investigations with a view to reducing its cost, and it has fallen from £300 per ton just after the war to its present level of less than one tenth this figure, largely owing to the production of synthetic methyl alcohol which is now used to the almost complete exclusion of the imported wood spirit hitherto employed. This cheaper source of raw material, coupled with greater efficiency in its conversion has enable formaldehyde now to be produced at prices which permit its use in agriculture and other processes where price is of supreme importance.

Some of these processes, which are of general interest, are briefly outlined in the remainder of this booklet, which is a short review in alphabetical order of the more important industrial applications of this versatile chemical, while more technical data as to chemical properties and approved methods of testing will be found in the appendix.

 **AGRICULTURE.** The advantages of formaldehyde as a soil steriliser have long been known, but it has only become widely used during the last few years, when reduced prices made its employment far more attractive.

Formaldehyde is also acknowledged the best remedy for red rust, and has the advantage over Sulphate of Copper, Sulphate of Potassium, and Jensen's warm water processes, in that it is less expensive and, moreover, does not impair the value of the cereals as foodstuffs.

Professors Falke and Tabeuf's efforts have shewn that irrigation with formaldehyde by Dehne's disinfecting machine and subsequent rapid drying in Konig's apparatus yield seed grain which is perfectly free from red rust, of unimpaired germinating capacity and free from all trace of formaldehyde. In other cases, the grain was spread on the floor, sprayed with dilute formaldehyde, turned over with a shovel to ensure thorough mixing, and after an interval of seven hours, finally dried by shovelling. The advantage of this



successful method is that it requires no special appliances, and is accordingly within the reach of any small farmer.

Extensive experiments have been made in Wisconsin under the auspices of the Agricultural Station (Report No. 28, 2nd Ed., Feb. 1903), from which it will be seen that seed oats, which had not been treated with formaldehyde yielded a crop involving a loss of 10-20% due to red rust, whereas on fields sown with formaldehyde treated oats the loss did not amount to 1%. On the basis of these experiments it is argued that the general adoption of the method of disinfection by formaldehyde would save the State 5 million dollars annually.

The process of disinfection is extremely simple. The seed corn is put into sacks and these are dipped for a period of ten minutes into a solution of $3\frac{1}{2}$ parts of formaldehyde (40%) in 1,000 parts of water. The sacks are then withdrawn, allowed to drip for 1-2 mins. and spread upon a drying floor. Drying is promoted by repeated shovelling, but there is no need to remove the last trace of moisture.

Formaldehyde a Remedy for Potato Disease.—The Wisconsin Agricultural Station has also found formaldehyde to be an excellent means for the suppression of potato diseases. The seed potatoes are placed uncut in sacks and suspended for two hours in a solution of 5 parts of 40% formaldehyde in 1,000 parts water. Potatoes treated in this manner yielded a crop which did not contain more than 5% of diseased potatoes as against 19% in the case of potatoes which had not been so treated. See also "Horticulture."

 **ALBUMINS.** Formaldehyde possesses the very remarkable property of coagulating albuminoids and converting them into insoluble and very stable compounds. All protein substances are converted into hard elastic masses, insoluble in water. As an example of this property it is interesting to note that an egg becomes "hard boiled" after an hour's immersion in 40% formalin solution.



● **ANTHRAX.** Formaldehyde has been found to be the best agent for disinfecting wool, hair, etc., to destroy the deadly anthrax bacillus.

A wool disinfecting station has been erected at Liverpool in connection with the Anthrax Prevention Act of 1919, and has an output of 40,000 lbs. of wool per week, the handling of the material being entirely automatic. The wool and hair is fed by a moving belt through alkaline solutions at 102°F. and soap solution at similar temperature to remove grease. It afterwards passes through rollers into the disinfecting machine where it is passed through two baths of 2.3% formaldehyde at 106°F. Subsequent to this, after passing through rollers, it is blown by air into a drying machine whence it is discharged into a cooling plant and re-baled.

Formaldehyde has also found much favour as a disinfectant for cattle trucks where anthrax may be suspected.

● **BARREL LINING.** Formaldehyde is used in an ingenious patented process for lining barrels, particularly those intended for the brewing trade.

The casein lining is produced by swilling the barrels for some time with a slightly ammoniacal solution of casein (glue or gelatine solution) mixed with a little formaldehyde and allowing it to drain. The barrel is then dried by blowing in warm air, after which it is rinsed with formaldehyde solution so as to render the coating of casein completely insoluble.

The lining, being absolutely impervious, prevents the escape of carbonic acid, it does not become detached from the side-boards, and, being quite insoluble, does not affect the taste of the beer. Having antiseptic properties, the formaldehyde-casein lining tends to preserve both the contents of the barrels and the barrels themselves. The lining is insoluble in alcohol, acids and alkalies. It may accordingly also be used for lining vessels holding fluids of the latter kind.



● **BLEACHING.** Sodium hydrosulphite, an important reducing agent used in the dyeing industry for the bleaching of wool and silk, forms with formaldehyde well-defined and stable compounds which can be used at high temperatures, and which only develop their reducing properties in the presence of acetic acid. An example of these compounds is zinc formaldehyde-sulphoxylate $\text{Zn}(\text{HSO}_2)_2(\text{CH}_2\text{O})_2$.

● **BREWING.** The extensive investigations of Professor Schwackhofer, Director of the Experimental Station and Brewing Academy of Vienna, have shown formaldehyde to be eminently adapted for disinfection in connection with brewing and other fermenting operations, especially in cases of obstinate infection. A valuable property of formaldehyde is that its presence in small quantities does not in the slightest degree affect the taste of the beer.

Superficial moistening of the fermenting and storing cellars, malt-floors, channels, etc., with 1 part of 40% formaldehyde per 100 parts of water suffices completely to eradicate micro-organisms, especially mould, and yields good results even where other media have proved unavailing.

Implements may be completely sterilised by dipping into, and washing with 1—2% formaldehyde. In this way fermenting vats and other vessels may, by thorough washing with formaldehyde solution, be protected from the invasion of mould, and an apparatus has been patented, specially adapted for washing and fumigating casks with formaldehyde solution or vapour.

Tubes, hoses, and pumps are rendered sterile by being kept filled for about 15 minutes with 2% formaldehyde and subsequent flushing with hot water.

The air in cellars is conveniently kept pure and free from atmospheric germs by interposing in the path of the air-current within the air channels, frames traversed by woollen threads dipping with one end in 40% formaldehyde and supplying the requisite fluid for evaporation on the principle of a wick.



Hops may be preserved successfully by the use of formaldehyde which possesses considerable advantages over sulphur. It does not, like sulphurous acid, bleach the tops or deteriorate the lupuline and other aromatic substances. Furthermore, the process is much simpler when formaldehyde is used, as the hops are simply sprayed with dilute formalin and immediately put into sacks.

● **CASEIN.** Objects made from casein or gelatine are rendered absolutely insoluble in water by treatment with gaseous formaldehyde or dilute solutions of this gas. Casein products are treated during manufacture by prolonged soaking in formalin solutions of about 5% strength in order to obtain a material which will be impervious to moisture. Such products as Erinoid, Galalith, etc., are manufactured from casein derived from milk which is hardened in this manner.

Solutions of casein are often used for lining casks, containers, etc., or for treating cardboard and papier mache. Formaldehyde is added to the solution and this ensures complete insolubility of the casein layer which, when dry, is quite waterproof.
See also "Barrel Lining."

● **COTTON PRINTS.** Dyes which are available for direct cotton printing, but are not sufficiently fast to stand washing with soaps, may be rendered fast on the fibre by treating the dyed cotton with formaldehyde.

● **COTTON SIZING.** Textures impregnated with albumen, casein, glue, gelatine or a mixture of these substances with coloured pigments, and other weight producing substances become charged with a perfectly insoluble size when passed through a 1-2% solution of formaldehyde or exposed to formaldehyde vapours.

● **DAIRIES.** The deterioration of milk and cheese is delayed even in the hottest season, and moulds are eradicated by thoroughly washing the vessels and other implements, as well as the walls and



floors of the dairies with 1—2% formaldehyde. Formaldehyde solution allowed to evaporate slowly from saturated pads will keep the air fresh and sweet.

DEODORANT. Formaldehyde is not a cover, but a true deodorant. Unlike perfumes which only mask evil odours, formaldehyde combines with putrescent material rendering it innocuous and preventing further decay, with the result that its action is positive and permanent. Solid and fluid substances are deodorised by suffusion with 1—2% formaldehyde, while only a small amount of vapour is required to purify the air. This may be obtained by the use of an atomiser filled with dilute (2%) formaldehyde solution or by allowing the solution to evaporate slowly from saturated pads or cloths.

Formaldehyde is thus eminently adapted for the deodorization of public lavatories, sewers, gutters, libraries, smoking rooms, damp cellars, mortuaries, waiting rooms, ship's holds, pantries, dairies, stables, tanneries, knackeries, bone mills, glue factories, etc.

DISINFECTANT. The disinfectant and bactericidal action of formaldehyde is due to its power of entering into combination with living protoplasm, or the albuminoid constituents of the germs, whereby it forms insoluble and devitalised substances which inhibit development of the organism and finally kill it by starvation.

The Rideal Walker Coefficient of 40% formaldehyde is 0.5 to 0.7 (*bacillus typhosus*) which means that formaldehyde gas is superior to carbolic acid as a disinfectant when used in solution. Formaldehyde, moreover, has many advantages over ordinary disinfectants of the carbolic acid and emulsion type, since unlike these fluids, the vapour or gas is as effective as the solution, and the penetrative qualities of the former (which has a density approximating to that of the air) enable confined spaces to be easily and thoroughly disinfected. Furthermore, formaldehyde solutions of the strength used for spraying purposes are non-poisonous and have the enormous



advantage of being harmless to most delicate fabrics or dyes, so that staining or bleaching cannot take place.

Infected dwellings, hospital wards, operating theatres, schools, barracks, prisons, mortuaries, etc., can be easily, cheaply and thoroughly disinfected by fumigation with formaldehyde, while for general use in the home it is unrivalled owing to its non-poisonous nature.

For ordinary domestic uses the commercial formaldehyde should be diluted with ten to twenty parts water, and if desired the slight odour, which, however, is quite harmless though somewhat sharp, may be masked by the addition of a little scent. This gives at very low cost a disinfectant which will meet all the ordinary domestic demands for drains, lavatories, and infected material. Cloths soaked in this solution will liberate sufficient formaldehyde by evaporation to keep pantries and rooms free from flies, at the same time exerting a definite preservative action where perishable food is concerned. The weaker solutions, when atomised and sprayed into the room, clean up the atmosphere to a remarkable degree, and remove the stale odours of tobacco smoke or the damp mustiness of a room rarely used.

A few spots in a glass of water form an excellent mouth wash and gargle, while soiled handkerchiefs can be effectively sterilised by an hour's immersion in 5% solution.

Further applications of this universal disinfectant will be found under other headings (Q.V.).

● **DISTILLERY.** Formaldehyde has proved extremely useful in combating moulds and other undesirable growths. Some comprehensive experiments by Dr. F. Rotherbach indicate that apart from hydrofluoric acid, formaldehyde is the only medium which enters seriously into consideration as a means of counteracting schizomycetes.

● **DYESTUFFS.** Formaldehyde, owing to its activity and the presence of a carbonyl group is of considerable importance in



the manufacture of both intermediates and dyestuffs. When formaldehyde is condensed with dimethylaniline tetramethyldiamine-diphenylmethane, an important intermediate is produced. Many dyestuffs are formed by condensing formaldehyde with amines. For example, Lithol Fast Yellow is obtained by condensation with chloro-6 nitroaniline.

● **EMBALMING.** Dr. Rechter has elaborated a method for the preservation of human and animal bodies by means of formaldehyde gas, which has met with much appreciation at the hands of anatomists and exponents of forensic medicine.

● **FABRICS Creaseless.** Many efforts have been made by textile manufacturers to obtain a fabric which will not crease after crushing. This problem has recently been solved and there are fabrics now on the market which will not crease however roughly they are treated, and in the process which overcomes this difficulty, formaldehyde plays an indispensable part.

● **FOOD PRESERVATION.** Formaldehyde has been used extensively as a preservative for perishable foodstuffs, and being 60 times as effective as boric acid in this direction, very minute quantities suffice for preservation purposes. Having entered into combination with organic matter it ceases to react as formaldehyde and becomes innocuous.

Meat, eggs, and vegetables may, even in the hottest season, be kept sweet by covering the vessel containing them with cloths soaked in or moistened with a few drops of formaldehyde. The antiseptic vapour which forms in this way cannot possibly affect the quality and taste of the food. A trace added to fresh milk (one part in 10,000) will keep it sweet for a long period, as it inhibits the growth of undesirable bacteria.

Unfortunately, owing to the abuse of these properties, legislation has been introduced which seriously restricts the use of formaldehyde as a preservative. Recent researches by Professor Hehring,



however, especially with regard to formaldehyde in milk, may do much to overcome these prejudices, since the physiological effect of the formaldehyde is negligible compared with toxins, the formation of which it so efficiently prevents.

● **FORMAMINT.** This is the trade name for a preparation of lactose (milk sugar) containing a small percentage of formaldehyde.

● **FORMAN.** The trade name for chlormethylmenthyl ether $C_{10}H_{19}O \cdot CH_2Cl$, a useful drug formed by action of formaldehyde on menthol in the presence of hydrochloric acid.

● **FUMIGANT.** Formaldehyde is a most excellent fumigant as its vapour is as effective a germicide as its solution, whereas carbolic acid vapours are entirely ineffective in cases even where the solution acts as a germicide. Saturated steam is the only medium which possesses a disinfecting power comparable to formaldehyde, but it has obvious disadvantages owing particularly to its disastrous effects on the appearance and colour of objects into which it comes in contact. Formaldehyde does not bleach the most delicate colours or in any way damage draperies, wall-papers or furniture.

For complete eradication of the most resistant pathogenic organism the room should be completely sealed and the formaldehyde vaporised by heating in a suitable vessel. For each 1,000 cubic ft. of room space Professor Flugge recommends $2\frac{1}{2}$ -oz. formaldehyde gas with $1\frac{1}{2}$ pints water. This is equivalent to 6-oz. of 40% formalin diluted to $1\frac{1}{2}$ pints. The water is added in order to assist the vaporisation and thorough diffusion of the formaldehyde gas and the water vapor also considerably increases the effectiveness of the germicide. The solution is boiled to dryness over a suitable lamp, the room being left sealed for five or six hours after which it can be thoroughly ventilated to disperse the gas.

Railway rolling stock can be perfectly disinfected by this means, and the Great Western Railway Company has recently introduced



at its Swindon Works a new type of apparatus for purifying the interiors and upholstery of rolling stock. This apparatus consists of a steel cylinder 85-ft. long and 16-ft. 6-in. diameter, provided with a track upon which the vehicles to be treated are run in without it being necessary to dismantle them in any way. The cylinder is then sealed by an airtight door swung into position. The temperature in the cylinder is raised to 120°F. by steam-heating pipes, which completely encircle the vehicle under treatment, and the air is withdrawn from the cylinder by a pump, until a vacuum reading of 28-in. of mercury is reached. This temperature and vacuum are maintained for six hours, ensuring complete purification. In cases where the vehicles have been exposed to infectious diseases, the above-mentioned temperature and vacuum is produced, and formaldehyde is then introduced into the cylinder from a small tank connected by a pipe to an evaporating chamber on the steam-heating pipeline, where it becomes formaldehyde gas and is drawn through perforated tubes into the cylinder, and when the vacuum is destroyed, penetrates to every part of the vehicle.

For ordinary domestic fumigation Paraformaldehyde is often preferred as it is easier to handle and a large number of proprietary fumigating lamps are on the market which make use of this material. They usually take the form of a tinplate container for the Paraform which rests over a small candle or night light. The Paraformaldehyde is generally supplied in the form of tablets (15 grain) so that the exact quantity of formaldehyde used can be easily gauged. The Paraformaldehyde easily vaporises and volatilises at temperatures exceeding 170°C. but its effectiveness can be improved upon by using it with water, which increases its bactericidal power.

 **HORTICULTURE.** It is now generally recognised by all Growers that periodic sterilisation of the soil is essential if the best results are to be obtained, especially in glasshouse soils, and for this purpose formaldehyde has proved to be the most efficient of liquid sterilisers, giving a high degree of control over all fungoid diseases.



As compared with the old-fashioned steaming it gives quite as good results without expensive plant and with a fraction of the time and labour hitherto necessary.

Sterilisation with formaldehyde ensures an effective control of the following destructive diseases :—

Damping-off or Blackleg of Seedlings (*Rhizoctonia solani*, *Phytophthora cryptogea* & *Phytophthora Parasitica*). Damping-off of Cucumber Seedlings (*Phthium de Baryanum* and *Colletotrichum oligochætum*). Foot and Collar Rots of Tomatoes (*Phytophthora* and *Verticillium*). Wilt diseases (*Fusarium Lycopersici* and *Verticillium wilt*). Stem Diseases (*Sclerotinia sclerotiorum*). Club root. Brown Rot (*Pseudomonas solanacearum*). Soft Rot of the Arum (*Bacillus Carotovorus*). Basal Rot of Bulbs.

Seed Sowing and Potting. Formaldehyde is invaluable for treating soil heaps for seed sowing or potting. In addition to immunity from disease, it gives considerably increased germination to such soft seedlings as Asters, Stocks, Broccoli, Cauliflower, Tomato, and similar fruit, flower and vegetable plants. It should never be forgotten that the spores of disease are present on the walls, paths, woodwork, and glass of the houses, as well as on the tools, boxes, pots and staging, and all these must be dipped or sprayed with formaldehyde to prevent re-infection.

Formaldehyde for the purpose of soil sterilisation should be used at a 2% dilution; i.e., one gallon formaldehyde to 49 gallons water, the dilute solution being applied at the rate of 50 gallons to every 20 square yards. The soil should be well turned over and no planting done until all traces of the formaldehyde have vanished. This is best ensured by permitting the soil to dry out thoroughly, and then allowing to stand, with occasional turning over, for three to four weeks if possible. It must be remembered that formaldehyde, owing to its activity has a strong retarding action on plant growth and may kill, even in small concentrations, so that every precaution should be taken to eliminate it before planting takes place.



"STERIFORM" a product of Pan Britannica Industries Limited of Waltham Abbey, Hertfordshire, is composed largely of SYNTHITE Formaldehyde, and is specially prepared for use in Agricultural and Horticultural work.

 **LEATHER TANNING.** Formaldehyde is largely used for tanning purposes, especially for sole leather. By its action on proteid bodies it makes the leather hard and firm without having the bad effect of acids.

Formaldehyde hardens swollen and unswollen leather, fixing it in either condition, and is accordingly employed as a means of producing permanently hard and stiff leathers, whereas leathers hardened during the process of swelling with acids are not permanently hard.

Formaldehyde hardens only, it does not produce swelling, but it exercises its grain hardening influence both upon unswollen hides as well as hides treated with acids. In the latter case it fixes the swelling accordingly. It is recommended that the hides should be first swelled with acids in the usual way and then suspended for 24-48 hours in a bath of formaldehyde containing about 2 litres of 40% formaldehyde per 1,000 litres. Leathers required to retain their grain are hardened by exposing the corium for 6-12 hours to the action of weak baths of formaldehyde (say $\frac{1}{2}$ litre 40% formaldehyde per 100 litres water).

It was first used for tanning by Payne and Pullman in 1908, who employed the following process. The prepared skins were soaked for several hours in a dilute solution of formaldehyde containing sodium carbonate, washed and treated with a solution of ammonium sulphate and dried. The leather obtained by this process has the appearance of chamois leather, but is whiter in colour. Griffith ("Leather Trades Review," 1908) replaced sodium carbonate by other salts such as sodium thiosulphate, sodium bisulphate or alum, whilst Thuau ("Collegium," 1909, 211) found that any compound capable of forming colloidal polymerides with formaldehyde could



be employed. The theory of formaldehyde tanning has formed the subject of considerable discussion. Nierenstein considered the phenomenon to be similar to that which takes place in oil tannage which is known to be a process of oxidation, accompanied by the formation of acrolein. Ropecky attributed the tanning action of formaldehyde to an emulsifying action of the natural grease on the skin. This emulsified grease being the true tanning agent.

The advantage of the prior use of formaldehyde is that the skin may be tanned subsequently in a much shorter time and with comparatively concentrated solutions of natural tannins.

 **MALTING.** Irregularities due to the presence of fungi are effectively overcome by steeping the barley with water containing formaldehyde. This treatment has proved particularly beneficial in cases where the material consisted of barley rendered bad by exposure to rain. In this connection it is specially interesting to note that formaldehyde does not in any way interfere with the germinating power of the barley.

Investigations of the diastatic qualities of malt have shown malt treated with formaldehyde to be much superior to one which has not been so treated. Exposure for two hours of the malt to the influence of a 2% dilution of the commercial 40% formaldehyde and subsequent washing with water are described as efficient means of effecting fermentation of an ideal degree of purity.
See also "Brewing."

 **MEDICAL.** In addition to the sterilisation of surgical instruments and the preservation of anatomical specimens, formaldehyde is used extensively in medicine, both directly, and in the form of compounds such as tannoform, forman, formatol, etc.

Weak solutions of formaldehyde ($\frac{1}{2}$ -1%) in conjunction with alcohol or glycerine have been recommended for treatment of abscesses and other infected tissues, particularly those of tuberculous origin.



Formaldehyde has also been used successfully for treatment of dental caries and as a prophylactic of corneal ulcers and corneal opacities, while inhalations of formaldehyde are excellent for whooping cough and nasal catarrh.

Compounds of formaldehyde with gelatine, dextrine, casein, starch, menthol, etc., are used for treatment of wounds, while dilute solutions of formaldehyde, or compounds of formaldehyde and tannin (Merck's Tannoform) for reliable anhydrotics.

 **PAPER.** Formaldehyde is an excellent medium for the cheap production of impervious paper, impervious cardboard ware, cartridges, art papers presenting a delicate surface, washable paper linen, washable wall paper, etc.

For this purpose the paper or paper articles are coated with casein solution (glue, gelatine) containing a small quantity of formaldehyde and then dried by the air.

 **PARAFORMALDEHYDE (PARAFORM).** A white powder consisting of a mixture of formaldehyde polymers. It has an indefinite melting point of about 160°C . and sublimes below this temperature. Commercial Paraformaldehyde is sometimes known as trioxymethylene though the latter term should, strictly speaking, only be applied to $\text{C}_3\text{H}_6\text{O}_3$ which is present in comparatively small proportion in paraform.

Paraform is used principally as a fumigant and disinfectant, and for this purpose is usually supplied in the form of 15 grain tablets. These are vaporised in a simple type of lamp consisting of a tin tray holding the requisite number of tablets over a small candle flame. (See also "Fumigant.")

The powder finds applications in medicine and also to a limited extent in industry for the preparation of special qualities of synthetic gums and resins.



● **PHOTOGRAPHY.** Formaldehyde is extensively used in place of alum as a hardening agent. The gelatine film on plates, films and papers becomes insoluble even in hot water after treating with 5% formaldehyde. This is extremely useful for photographic work in the tropics and it has the added advantage that the silver image, either latent or developed, is quite unaffected by the treatment.

● **RESINS.** The manufacture of synthetic resins has developed at an astonishing speed during the last few years, owing chiefly to the rapidly increasing demand for moulding powders and varnishes.

When formaldehyde is condensed with phenols, resins can be produced which have the unique property of being fusible and soluble under normal conditions, but which, after heat treatment become insoluble, infusible and practically inert under any chemical treatment.

When mixed with suitable fillers such as paper pulp or wood flour, moulding powders can be made which when forced into hot moulds under high pressure will reproduce intricate shapes with comparative ease. After removal from the mould the object is fully hardened and will not distort even under the most trying conditions of high temperatures or strain, and it is furthermore not influenced in the slightest degree by moisture or chemical action. These mouldings are finding extensive use for domestic and electrical purposes since the material has the added advantage of being an excellent insulator, both for heat and electricity. Such items as knobs, switch covers, wireless and magneto parts and even cabinets are now being manufactured in this way, while if urea or thiourea is substituted for phenol, translucent mouldings of brilliant colours can be made and these are now being widely used for tableware and ornamental work.

The pure resins when blended and mixed with suitable solvents form varnishes with many valuable and unique properties, the principal one being that of hardening to a completely resistant film after stoving. These varnishes, owing to their infusibility and high insulation resistance of the film, are used extensively in the electrical industry.



By coating layers of paper with one of these thermo setting resins of the phenol-formaldehyde type, and subjecting a pack of this impregnated paper to hydraulic pressure, a laminated insulating material of very great strength, both electrical and mechanical, is obtained.

A similar but tougher product can be formed from blocks of impregnated canvas which are in considerable demand for pinions and other gear wheels where silent operation is desired.

This material, in view of its lightness, is now being used for the manufacture of miners' shockproof helmets, and there is little doubt that before long even motor car bodies and elaborate furniture will be fabricated from this versatile substance.

Chemical plant is also being constructed from laminated material and it is as resistant to corrosion as earthenware without the fragility and uncertainty of the latter.

RUBBER. Formaldehyde solution is sometimes used for coagulating latex, and the curing of rubber over wood fires is ascribed in part to the presence of formaldehyde in the smoke.

SILK. Formaldehyde has been used effectively as a means of disinfection to combat the ravages of the dreaded lime disease among silkworms.

It has also been used in the actual silk manufacture, since by treating the fibre first with gelatine or albumen solution and afterwards immersing in 5% formaldehyde or exposure to formaldehyde gas, the silk acquires an increase of weight amounting to 40 or 50%.

Natural silk, being an animal textile fibre consisting chiefly of proteins reacts with formaldehyde in a manner somewhat similar to hide. When raw silk is soaked in a dilute solution and dried, the sericin becomes insoluble in cold or moderately hot water, and only dissolves comparatively slowly at boiling point. The dyeing properties, however, are not affected and hence it can be dyed without loss of weight.



● **SIZE.** Solutions of size and glue rapidly turn sour when kept a few hours, but this decomposition can be completely prevented by the addition of a little formaldehyde to the solution. Four ounces of 40% formaldehyde will be found sufficient to keep 60 gallons of size in perfect condition for a long period. It is important to note that in the case of coloured sizes or distempers, formaldehyde has no appreciable effect on running colours, whilst it has absolutely no effect on fast colours.

● **SPECIMENS.** Anatomical or museum specimens may be preserved very satisfactorily in 2% formaldehyde solution. It does not extract chlorophyll or bleach haematin in the presence of alcohol, but it fixes permanently both animal and vegetable tissues, and is largely used in museums for preserving exhibits of this character.

● **STABLES.** Formaldehyde is an excellent air purifier for stables. It reduces sulphuretted hydrogen and ammonia and dispels the dense foul atmosphere speedily and permanently. Furthermore, it is harmless to animals, and, providing it is not used too strong, does not incommode them in the least, moreover, it protects them from flies.

● **TANNING.** Closely related to synthetic resins are "Synthetic Tans" which are employed to a considerable extent in the manufacture of certain kinds of leather. The first of these, termed Neradol, was discovered by Stiasny who made it by heating cresol with an equal quantity of sulphuric acid for some hours at a temperature of from 100°C. to 120°C. and then, whilst cooling, stirring in one molecule of formaldehyde to every two molecules of phenol used. Finally the free acid was neutralised by means of sodium hydroxide. Neradol is thus a sulphonated condensation product of a phenol with formaldehyde. Stiasny's discovery aroused great interest and led to the preparation of many similar compounds. When analysed by the hide powder method, Neradol gives 32% of tanning matter. It produces a white leather, somewhat similar to



that obtained with sumac. It has, however, not so great a filling power as vegetable tannins and is used chiefly in conjunction with the latter.

● **TAR OILS.** Formaldehyde has been suggested as a means of removing carbolic odours from tar oils (patented) by mixing with formaldehyde in the presence of an acid or alkaline catalyst and blowing with steam.

Formaldehyde has also been used for the elimination of bodies which cause the pink coloration of tar oil emulsions.

● **WATERPROOFING.** Waterproof dressing for textile fabrics, straw hats, etc., often consists of formaldehyde-gelatine or casein. The goods are passed through a dilute aqueous solution of gelatine, dried, and then exposed to formaldehyde vapour or passed through a weak solution of the gas.



APPENDIX

Formaldehyde $\text{H}\cdot\text{CHO}$ is the first aldehyde of the aliphatic series, and though it possesses many properties of aldehydes in general it differs from the rest of the series in several important characteristics.

With ammonia, instead of forming the usual additive compound, it combines fiercely and quantitatively to form hexamethylene tetramine $(\text{CH}_2)_6\text{N}_4$, a ring compound of considerable stability. It is a crystalline substance, very soluble in water, slightly so in alcohol, and is used in considerable quantities in the manufacture of synthetic resins and is also employed extensively in medicine.

When formaldehyde is boiled with alkalies such as lime, it readily polymerises and condenses into sugar-like bodies, and on evaporation these are obtained as a sticky mass of considerable complexity.

Formaldehyde reacts with most organic and many inorganic substances, the extreme activity and presence of a carbonyl group enabling it to be employed in many organic syntheses, while its strong reducing properties also render it valuable in other applications.

The gas is extremely soluble in water, a solution saturated at ordinary temperature containing approximately 50%; such a solution, however, is not stable, especially in the absence of any alcohol, and hydrated paraformaldehyde is rapidly precipitated. Ordinary commercial 40% formaldehyde is the strongest solution which can be handled satisfactorily without fear of undue polymerisation. It is however, questionable as to the actual $\text{H}\cdot\text{CHO}$ which normal "40% formalin" contains, since the molecules so readily associate, and there is undoubtedly a large proportion of diformaldehyde or methylene glycol, $\text{CH}_2(\text{OH})_2$ present in solution, together probably with a number of hydrated higher polymers as well.



Fortunately, these react generally as formaldehyde and can usually be ignored, but they may have some influence on more intricate processes, and the chemically heterogeneous nature of ordinary formaldehyde solutions should be kept in mind.

The proportions and composition of these polymeric forms is probably determined by the initial method of manufacture and also to a lesser extent by the time and temperature of storage, while the amount of alcohol and impurities present are also certain to have some effect.

When formalin is evaporated to dryness, a white mass of polymerised formaldehyde is obtained, which, when reduced to a fine powder, forms the paraformaldehyde of commerce. This consists of a number of complex polymers $(\text{CH}_2\text{O})_n$ together with hydrated forms $(\text{CH}_2\text{O})_n \text{H}_2\text{O}$, where "n" is probably 6 to 8.

When evaporation is carried out in the presence of a dehydrating agent, the principal product obtained is trioxymethylene $(\text{CH}_2\text{O})_3$, a definite crystalline compound fusing at $171-172^\circ\text{C}$., and insoluble in water, alcohol, and ether at ordinary temperatures. Much work has been done on the various polymers of formaldehyde, Auerbach and Barschall claim to have established the identity of at least six Paraformaldehydes $(\text{CH}_2\text{O})_n \text{H}_2\text{O}$; four polyoxymethylenes $(\text{CH}_2\text{O})_n$ and Trioxymethylene $\text{C}_3\text{H}_6\text{O}_3$ of ring structure. Commercially, both trioxymethylene and paraformaldehyde are synonymous terms though from a strictly chemical point of view this confusion is deplorable. The paraformaldehyde generally marketed is a mixture of partly dehydrated polymers containing 95—97% "formaldehyde" the remainder being loosely combined water which it is not economic to remove.



METHODS OF TESTING

● **FORMALDEHYDE.** Formaldehyde solution should be clear and water-white, the specific gravity usually being, in the case of 40% material, between 1.088 and 1.095 at 15°C. It should be noted that formaldehyde increases, and methyl alcohol decreases the specific gravity, so that this is no criterion of quality.

Estimation of Formaldehyde. Several methods of estimating the formaldehyde present in solutions have been suggested but the simplest and most reliable is that given by the British Pharmacopœia which is based on the oxidation of formaldehyde to formic acid by hydrogen peroxide, the acid being neutralised by standard sodium hydroxide. The technique of the test briefly is as follows :—

Take 3 cc. of the solution to be tested and add to 50 cc. normal sodium hydroxide in a 300 cc. conical flask. Add to this 50 cc. neutral hydrogen peroxide (10 vol.) and agitate flask to mix thoroughly. Place on water bath for 20 minutes to complete the reaction and remove excess H_2O_2 . Allow to cool and titrate back with normal sulphuric acid. Phenol phthalein may be employed as the indicator, but should then be used for standardising all solutions. The number of cc. soda used gives the percentage formaldehyde on the "volume" basis directly, and the percentage by weight can obviously be easily calculated by dividing the result obtained by the Specific Gravity of the solution. When the formaldehyde content and Specific Gravity of the solution have been determined the alcohol can be estimated from the three co-ordinate graphs on opposite page.

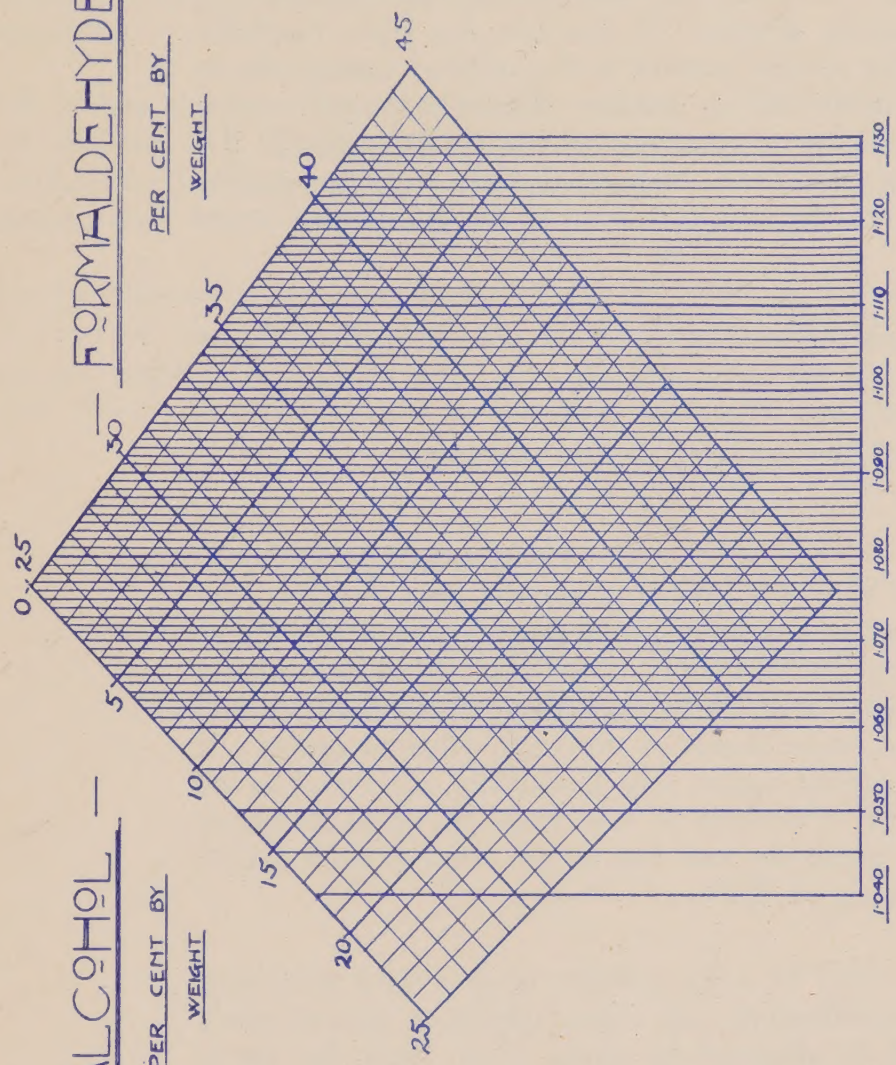
Estimation of Alcohol. The direct estimation of alcohol in formaldehyde solution present some difficulties and the following method is often employed, though its accuracy is probably not very high :—

Take 50 cc. of the formaldehyde solution to be tested and place in 300 cc. conical flask. Keep well cooled in running water



— ALCOHOL — FORMALDEHYDE —

PER CENT BY WEIGHT



— SPECIFIC GRAVITY AT 15.5°C. —



and add slowly with constant shaking a mixture of 35 cc. .880 ammonia diluted to 100 cc. with water. Allow to stand in tightly stoppered flask for 6 hours. Distil off as much of the liquid as possible (about 120cc.), acidify the distillate with sulphuric acid and redistil. Collect 50 cc. first fraction and determine its specific gravity. If the test has been carefully carried out, all the alcohol present in the original formaldehyde solution will be in the 50 cc. fraction diluted only with water, so that as this fraction is equal in volume to the original, the alcohol percentage can be determined directly from the density by reference to specific gravity tables of methyl alcohol-water mixtures.

It will be obvious that the tests given above refer primarily to pure solutions of commercial strengths and they may not be applicable to manufacturers' solutions where the presence of other substances might adversely affect the accuracy of the estimation.

 **PARAFORMALDEHYDE.** Paraformaldehyde should contain not less than 95% HCHO , and usually tests 96-97%, the residue being moisture in a state of weak combination. The Paraformaldehyde sold by SYNTHITE LIMITED is of particularly high quality containing over 96% equivalent formaldehyde, and fully conforms to the requirements of the U.S. Pharmacopœia. It is slightly soluble in cold water, but practically all dissolves on boiling. SYNTHITE Paraform is free from all traces of heavy metal or deleterious impurities and has an ash content much below the stipulated maximum of 0.1%.

It is supplied in the form of a fine powder or in a semi-granulated condition for tablet manufacture, and also as tablets of approximately 15 grains weight ($\frac{5}{8}$ -in. diameter by about $\frac{1}{8}$ -in. thick) for use in fumigating lamps.

It may be assayed in a similar manner to that described for 40% formaldehyde by substituting 1 gram of the powder for 3cc. of the solution to be tested.



1 cc. normal soda = .003 grams formaldehyde. In addition to the formaldehyde estimation it is usual to volatilise completely about 10 grams of the paraformaldehyde in a tared crucible which is afterwards reweighed to obtain the ash content. This should not exceed 0.1%, and will usually be found to be far below this maximum.

On boiling a gram of paraform in 10cc. water, it should practically all dissolve and the solution should give negative reactions with sulphuretted hydrogen (absence of heavy metals) and Barium chloride (sulphates).

If any difficulties are experienced or further technical information is required the chemical staff of SYNTHITE LIMITED are always eager to assist and place their experience at the service of their clients.



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